

## PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

## Improvements in and relating to Closure Means and Seals for Bottles, Cans and other like Containers

We, NATIONAL CARBON COMPANY, INC., of 30, East 42nd Street, New York, State of New York, United States of America, a corporation organized and existing under the laws of the State of New York, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The present invention relates to performed articles for use as closure seals or closure protectors, and to the method 15 of making such articles. More particularly, it relates to such articles preformed as an expanded tube or a drawn rod and formed of a material adapted to change its size upon treatment.

20 Said articles are especially adapted to be used for protecting containers against the unauthorized removal or the adulteration of the contents thereof, making it necessary in order to remove the closure to inflict permanent readily observable injury to said article.

The invention has particular utility 25 in connection with the provision of tamper-proof seals for protecting the closures of containers of various kinds, such as bottles, cans, and the like, containing distilled and other liquors used for beverage purposes.

Articles for closure seals comprising 30 an expanded tube preforms have previously been proposed made of a celluloid material, such articles being placed upon the bottle or vessel to be closed and then heated by placing in hot water or by treating with steam or the like, whereupon the cap contracts onto the neck of the bottle or vessel.

According to the present invention the material of which said preform is made 45 comprises a thermoplastic resinous composition having a vinyl resin as a base, such composition being in a heat unstable condition having internal strain, and being adapted, upon said treatment, 50 to changing its shape, to have said strain decreased or removed and to change to a heat stable condition.

The thermoplastic resinous composition which is used according to the present invention may be said to exist in two primary states, hereinafter designated as "heat-stable" and "heat-unstable". The term "heat-stable" is used to describe that condition of the resin or composition in which all of the internal elastic forces are released and are in equilibrium. In this condition the composition will not alter its physical form upon the application of heat until its plasticity becomes so great as to approach fluidity and thus allow it to distort by pure flow. The term "heat-unstable" indicates that condition of the resin or composition in which the elastic forces are not all released or balanced but are retained in the material due to its rigidity at temperatures below its heat-distortion point. From this heat-unstable condition, the composition upon the application of heat above its heat-distortion point, changes irreversibly and automatically in physical form or shape into that form or shape in which the internal elastic forces will be released or will be at a minimum value. The terms "heat-stable" and "heat-unstable" as herein used do not refer to the chemical stability of the material, but rather to the state of the physical forces within the mass.

The thermoplastic resinous compositions which are used according to the present invention are convertible into heat-unstable shapes by mechanically altering the shape of a given mass of the material at any temperature below that at which the material approaches fluidity. It then may be converted from the heat-unstable into a heat-stable condition in various ways, as by the application of heat in practically any degree.

Among the more important objects of the invention are: to produce in novel manner a tamper-proof container seal which may be readily applied to a closure, and which cannot thereafter be removed without readily-observable, permanent injury to the seal; and to provide a novel container seal of attractive appearance, which per se is adapted to

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serve as a closure that can be removed only upon its injury or destruction.

In carrying out the present invention a heat-unstable preform is formed from the resinous composition; and, a heat treatment or the equivalent is given the preform, which irreversibly converts the preform into its final shape and renders it heat stable. Vinyl resins and compositions having as a base vinyl resins have odorless, tasteless, permanency and insolubility characteristics. They are also colorless and container seals prepared therefrom may be provided in any desired color or color-pattern by suitable means. Throughout the specification and claims the term "vinyl resin" is intended to designate those products which may be made by the polymerization of one or more vinyl esters, or mixtures containing vinyl esters and vinyl benzene. It is preferred to employ in the practice of the invention vinyl resins resulting from the conjoint polymerization 25 of vinyl halides and vinyl esters of organic acids, in the proportion of about 70% to about 95% of vinyl halide, and of these latter products those which may be made with vinyl chloride are preferred. These resins may be modified by the incorporation of substances adapted to increase the stability of the resins to light and/or heat, such as urea and calcium stearate. Lubricants such as 30 carnauba wax and halogenated naphthalenes may be employed where the composition is to be extruded; and other substances may be incorporated with the resin, such as wood flour, silica, asbestos, and other filling materials; and colored 35 pigments and dyes.

In the accompanying drawing, illustrating the invention,

Figure 1 represents, in vertical section 45 a bottle closure or cap embodying the invention;

Figure 2 represents, in vertical section the cap sealed in position on a container neck;

Figure 3 illustrates in section a closure cap sealed in place on a container having a screw-threaded neck;

Figure 4 is a section through a tubular closure seal;

Figure 5 illustrates in section the tubular seal of Figure 4 sealed in place upon a closure;

Figure 6 illustrates in section a rod-like closure member having a surface 60 layer of resinous composition;

Figure 7 illustrates in section the closure member of Figure 6 in expanded form in a bottle neck;

Figure 8 illustrates in vertical section 65 another modification of the invention

utilizing a locking member or key; and Figure 9 is a horizontal section taken along the line 9-9 of Figure 8, looking in the direction of the arrows.

In Figures 1 to 3, numeral 10 designates a cap or closure-sealing member made of the thermoplastic resinous composition. Figure 2 illustrates this cap shrunk in place on the neck of a container 12 having therein a cork closure member 14. Figure 3 is a view similar to Figure 2 and illustrates the cap 10 shrunk in place on a container 16 having a screw-threaded neck, illustrating the manner in which, upon shrinkage of the 80 cap, the latter conforms to the shape of the surface engaged thereby.

In the form illustrated in Figure 5, a tubular closure seal member 20 of resinous composition, (shown in heat-unstable 85 form in Figure 4), is shrunk tightly in place around both the neck of a container 22 and the side margins of a screw-threaded closure member 24, the latter of which may be formed of any suitable 90 material.

The closure-sealing member illustrated in Figure 6 comprises a rod having a core 26 of cork or other resilient material imbedded within, or having 95 thereon a surface layer, body, or coating, 28 of resinous composition in heat-unstable form. The length and diameter of the core can be varied within wide limits. Figure 7 shows the rod of 100 Figure 6 expanded in the neck of a container 30. In the form shown, the portion of the rod extending above the top of the container is fully expanded and in heat-stable form. The balance of the 10 resinous composition may be either in heat-stable form, or in more or less of a condition of internal strain, in either case providing a tight seal.

The closure member illustrated in 111 Figures 1 to 3 may be produced by molding under high pressure a hollow preform of a resinous material of the nature herein described, which, upon removal from the mold or press, has its internal cross-sectional area or diameter enlarged by suitable means, and is chilled while in this expanded form. This enlargement may be accomplished by means of a mandrel or other suitable device while maintaining the resin composition near but below the heat distortion point, and thereafter quickly chilling the shaped preform.

The tubular closure-seal member illustrated in Figures 4 and 5 may be produced by extruding a vinyl resin composition of tubular form and, while the same is hot, enlarging its diameter, and thereupon chilling it in its expanded 12 13

heat-unstable form. This increase in diameter may be effected by applying fluid pressure to the inside of the tube confining the latter within a matrix of the desired size.

Where extrusion methods are used, the temperatures and pressures within the extrusion device may vary widely. Temperatures around 100° C. to 140° C. and pressure from 1000 to 10000 pounds per square inch have been found very satisfactory. The heat distortion points of the vinyl resins used generally range around 56° C. to 70° C.

In the form of the invention illustrated in Figures 6 to 9, a vinyl resin or other resinous composition to be used may be extruded in the form of a rod having a solid or a tubular core of suitable material, preferably a yieldable material such as cork, or a resilient material such as rubber, surrounded by and/or containing a layer or body of the said resin composition in heat-unstable form. The extrusion produces a rod of considerably larger cross-section than that of the aperture through which the extrusion occurs.

Where an elastic material such as a rubber composition is used as the core, the tubular layer or body of vinyl resin, upon being chilled, not only itself contains strains which when released cause an increase in its cross-section, but due to its strength and rigidity in the chilled state, the cold resin maintains internal strain within the rubber core, particularly in instances where the rod is drawn or stretched during the process of its formation. Upon heating the resinous body to expand it, the resultant loss of strength permits the rubber core to change its shape in a like manner, becoming shorter and thicker.

The said rod may be made entirely of the said resinous composition if desired. Thus a vinyl resin composition may be extruded through a die having a discharge opening of such size that a continuous rod of the resin is formed, having an initial diameter of around  $\frac{1}{4}$  inch. While still warm, tension is applied to this rod of warm material, thereby stretching the rod until it has a diameter of about  $\frac{1}{2}$  inch. The rod then quickly

is chilled to around room temperature or below, while in this stretched condition. The stretching operation mentioned above is not always essential, but is desirable, since it increases greatly both the magnitude of the residual strains remaining in the chilled rod, and the degree to which the rod changes in diameter upon release of the said strains.

This chilled rod can be cut into sections and a section placed in an aperture to be

sealed which has a cross-section slightly less than that of the rod when in its final, heat-stable form. When the sealing member is heated,--preferably to above 75° C.,--the extruded preform or rod expands in cross-section inversely to assume the heat-stable position, thus filling the aperture and securely sealing the same.

The degree to which the extruded and chilled rod will increase in cross-section upon final heat treatment may be increased by the regulated stretching of the extruded rod while hot to reduce its diameter, in instances where no core is used, or wherein the core contains an elastic material such as rubber. The extrusion pressure, the rate of travel and the tension upon the tube leaving the extrusion device, and the rate of chilling of the extruded mass, are adjusted to control the amount of residual strain or degree of heat instability in the extruded material.

By increasing the feed pressure upon the thermoplastic material it is possible to increase the rate of production of the extruded material while maintaining the desired amount of residual strain or heat instability therein. Moreover, by controlling the rate of chilling of the said tube or rod, the degree of expansion occurring therein prior to cooling may be regulated, and, therefore, also the amount of residual internal strain in the tube 100 or rod.

In the form of the invention illustrated in Figures 8 and 9, a sloping groove 40 may be formed in a container outlet wall. A container screw cap or other closure 42 of suitable material, such as metal or a hardened plastic composition, has apertures 44, 46, in its top and side in alignment with the said groove. A tamper-proof cap seal is formed by inserting an 110 expandable rod 48 of vinyl resin or the equivalent through the apertures in the cap and within the groove, after which heat is applied to the rod to expand the same and lock the cap securely to the 115 container wall in obvious manner. The screw cap is thus locked in place, and cannot be removed from the container without breaking the rod 48.

It is preferred to produce the preformed 120 cap or tube of such size that, when secured in place on the object to be sealed thereby, all or the major portion of the residual strain therein has been released.

The following will serve to illustrate 125 the invention:

A vinyl resin, prepared by conjointly polymerizing vinyl acetate and vinyl chloride in the proportions of about 85% by weight of vinyl chloride and about 130

15% by weight of vinyl acetate, and containing around 3% by weight of carnauba wax and about 3% by weight of alkaline calcium stearate, was heated to around 5 125° C., and was extruded in the form of  $\frac{1}{4}$  inch internal diameter tubing from an extrusion device under a pressure of around 2500 pounds per square inch. The tube while hot, as it left the die of the 10 extrusion device, was expanded so as to have an internal diameter of  $1\frac{1}{2}$  inch and a wall thickness of .015 inch, by means of compressed air at 5 to 10 pounds per square inch applied to the 15 open end of the tube while the latter was supported within an encasing tube. The tube was quickly chilled in the expanded condition. Thereafter, a section of the resultant heat-unstable tube was severed 20 and was placed around the neck and closure member of a glass bottle. The latter was then subjected to heat around 100° C. for about 10 minutes, whereupon the rigidity of the material was reduced 25 sufficiently to permit flow thereof under the effect of the internal forces present in the heat-unstable mass. The tube then assumed the form and shape in which it was heat stable. This produced substantial 30 shrinkage of the mass, causing it tightly to adhere to the bottle neck and seal the closure in place. Since it is not possible again to develop in the mass the identical 35 conditions of heat instability, the closure could not be removed thereafter excepting by permanent deformation or destruction of the same.

Other means besides heat may be employed in certain instances to release part 40 or all of the internal strains present in the heat-unstable preforms and permit such flow of the material as converts the preform to the heat-stable condition. Thus, suitable volatile solvents or well 45 known medium-boiling and high-boiling softeners for the resinous material may be applied to one or both surfaces of the cap or preform before application of the latter to the closure, for the purpose of facilitating flow of the material and the release of part or all of the internal strains in the preform, at temperatures even as low as atmospheric temperatures or below.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

60 1. An article for a closure seal comprising a preform such as an expanded tube or a drawn rod, formed of a material adapted to change its size upon treatment characterized in that the material of 65 which said preform is made comprises a thermoplastic resinous composition having a vinyl resin as a base, such composition being in a heat unstable condition having internal strain, and being adapted, upon said treatment, to changing its 70 shape, to have said strain decreased or removed and to change to a heat stable condition.

2. A preform as claimed in claim 1 characterized in that the resinous composition is produced by the conjoint polymerization of a vinyl halide and a vinyl ester of an organic acid.

3. A preform as claimed in claim 2 characterized in that the vinyl halide is 80 vinyl chloride and the vinyl ester is vinyl acetate.

4. A preform as claimed in claim 2 or 3 characterized in that said resinous composition comprises about 70% to 95% of 85 the vinyl halide.

5. A preform as claimed in any of the preceding claims characterized in that substances are incorporated in said resinous composition which are adapted 90 to increase its stability to light and heat, such as urea and calcium stearate.

6. A preform as claimed in any of the preceding claims characterized in that fillers, such as wood flour, silica, asbestos 95 or the like are incorporated in the resinous composition.

7. A preform as claimed in any of the preceding claims characterized in that colored pigments and/or dyes are incorporated in the resinous composition.

8. A preform as claimed in any of the preceding claims characterized in that the internal strain is removable by the action of heat and/or a solvent.

9. A closure seal formed from a preform of the kind claimed in any of the preceding claims, either as a cap over the outer surface of the aperture or as a rod incorporated in a stopper or located inside 110 said aperture.

10. A method of producing the closure seal claimed in claim 9 in which the resinous composition is initially formed either into a cap or into a stopper preform 115 by chilling a hot expanded tube or a hot drawn rod of said resin, placing the resulting tube or rod preform over or into the aperture, and contracting said tube or expanding said rod by the application of 120 heat and/or solvent so as to snugly fit the walls of the aperture.

11. A method as claimed in claim 10 in which the resinous composition is a polymerized resin characterized in that 125 the cap or stopper preform is obtained by extruding the conjoint polymerized resin at a temperature from about 100° C. to 140° C. and at a pressure from about 1000 to 10000 pounds per square inch. 130

12. A method as claimed in claim 11 in which lubricants, such as carnauba wax and halogenated naphthalenes are incorporated in the resinous composition 5 prior to extrusion.

13. A method as claimed in claim 11 or 12 in which the extruded resin is either expanded or drawn and then chilled to a temperature below the heat distortion point which is from about 56° C. to 70° C 10 in order to produce the internal strain in the resulting preform.

14. A method as claimed in claim 13 in which the chilled resin preform after be-

ing placed over or into the aperture is 15 reheated to about 100° C. in order to decrease or remove the internal strain of said resin.

15. A closure seal as claimed in claim 9 substantially as described with reference 20 to Figures 1-3; 4 and 5; 6 and 7; or 8 and 9 of the accompanying drawing.

16. A method of producing a seal as 25 claimed in claim 10 substantially as hereinbefore described.

Dated this 10th day of January, 1936.  
MARKS & CLERK.

